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Time-resolved synchrotron X-ray diffraction study of the dehydration behavior of chalcophanite

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ABSTRACT

Time-resolved synchrotron X-ray powder diffraction data were used to investigate the dehydration behavior of the chalcophanite ($ZnMn_3O_7{\cdot}3H_2O$) structure from 300 to 1060 K. Rietveld refinements revealed two obvious phase changes, at ~450 and ~950 K, corresponding to the dehydration of chalcophanite followed by transformation to a spinel structure (Mn-hetaerolite). Only small changes were observed in the chalcophanite unit cell from RT to ~438 K; the volume increased by ~0.8%, mostly caused by thermal expansion of ~0.5% along *c*. Above ~427 K, the interlayer water molecules were lost, resulting in a collapse of the interlayer spacing from ~7 to ~4.8 Å. The newly formed anhydrous phase ($ZnMn_3O_7$) retained chalcophanite's $R\overline{3}$ space group and *a* dimension, but the *c* dimension decreased from ~21 to 14.3 Å, and the Zn coordination changed from octahedral to tetrahedral. Above ~775 K the anhydrous chalcophanite began to transform to a spinel structure, corresponding to a Mn-rich hetaerolite [$(Zn_{0.75}Mn^{2+}_{0.25})Mn^{3+}_2O_4$]. By ~973 K the transformation was complete. The diffraction patterns did not show a significant increase in background during the transformation, indicating that the reaction did not involve transient amorphization. The phase change was likely triggered by loss of 1.25 of seven O atoms in the original anhydrous chalcophanite structure with a corresponding reduction of Mn^{4+} to Mn^{3+} and Mn^{2+}.

Keywords: Chalcophanite, hetaerolite, birnessite, Rietveld, synchrotron